Solubility of silicon in liquid metal at high pressure: implications for the composition of the Earth's core

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Abstract

Silicon solubility in liquid Fe-rich metal was measured experimentally as a function of pressure, temperature and oxygen fugacity to determine if silicon could be a major light element in the Earth's core. At the P, T, fO_2 conditions of the experiments, Si solubility in liquid metal increases with increasing pressure, increasing temperature and decreasing oxygen fugacity. Evaluating single-stage core formation scenarios, the experimental results show that if the core segregated at low pressure (~ 2.5 GPa) and an oxygen fugacity consistent with the current FeO content (8 wt%) of the mantle, the liquid metal would contain negligible Si (< 0.01 wt%). If, as proposed recently [1–3] however, the metallic liquid equilibrated with the mantle at the base of a deep magma ocean (~ 700 km depth, 25 GPa) the experimental results suggest a core containing several wt% Si. For example, at the melting temperature of a peridotite mantle (~ 2800 K), which represents the temperature at the base of a magma ocean, 2 wt% Si (conceivably as much as 6 wt%) could dissolve in liquid Fe metal at 25 GPa. In order to generate a core containing 7 wt% Si, as required by the CI chondrite Earth model, a magma ocean extending to 850 km (28–30 GPa) would be required. We conclude therefore that equilibration at the base of a deep magma ocean is consistent with Si being a major part of the light element inventory of the core. Extrapolation to the core–mantle boundary pressure shows that the solubility of Si in the metal, after increasing in the upper mantle, decreases with increasing depth in the lower mantle due to the change of Si coordination number in solid silicates from 4 to 6. This result is in agreement with predictions based on theoretical arguments [4] and on EOS measurements of FeSi alloys [5]. Therefore, a core segregated at the base of a deep magma ocean and containing several wt% Si must now be back-reacting with the mantle, expelling Si and absorbing Fe from the silicate. Progressive reaction of this kind may, in part, be responsible for a chemical boundary layer represented by the D″ layer at the core–mantle boundary. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

The segregation of the Earth's metallic core from the silicate mantle was the most significant event in the chemical differentiation of the planet. It resulted in the core containing most of the Earth's inventory of 'siderophile' elements such

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as Fe, Ni and Co and a silicate mantle enriched in the refractory lithophile elements such as Ca, Sc, Ti and the REE [6]. Because the Earth's outer core is significantly less dense (by $\sim 10\%$) than Fe (e.g. [7]), the core must also contain about 10–15 wt% of one or more light elements, which were presumably dissolved into the metal during separation from the mantle. Although the identity of the light element(s) [8,9] is still uncertain, it is clear that it, or they, must be both cosmochemically abundant and soluble in liquid Fe under the conditions of core segregation. Therefore, the most likely candidates are S, Si, C, O and H [8,9]. The mantle of the Earth is depleted in Si relative to chondritic material, caused either by removal to the core or by volatile behaviour during the early history of the Earth. Assuming Si to be non-volatile and accepting the proposal of Allègre et al. [10], that the contents of non-volatile elements in the Earth approximate those of CI chondrites, then the relative depletion of Si in the mantle means that the dominant light element in the core is Si. In that case the core should contain about 7 wt% Si and, using similar cosmochemical arguments, 2 wt% S [10,11]. Si as a major component in the core has also been proposed by other authors, based on CI or other models for the bulk Earth composition (e.g. [4,12]). The hypothesis that Si is a major light element in the core has important implications for the chemistry of the mantle and the conditions of core segregation.

Recent experimental studies show that Si becomes siderophile only under very reducing conditions at low pressures and moderate temperatures [13,14]. At 2.5 GPa and 2023 K, for example, the core would have had to equilibrate with the mantle at an oxygen fugacity at least 5.5 log units below the Fe–FeO (IW) buffer in order to contain 7 wt% Si. Under these conditions, however, Fe, Ni and Co partition strongly into the metal (i.e. $D^{met/sil}$ values are high) and their concentrations in silicates are several orders of magnitude lower than those observed in the present-day mantle, thus precluding single-stage core–mantle equilibrium at very low oxygen fugacity [13]. The FeO content of the mantle (~ 8 wt%) would require that single-stage equilibration took place at an oxygen fugacity ~ 2 log units below the IW buffer (e.g. [15]). Under such redox conditions at low pressure, however, the Si content of liquid metal is negligible (< 0.01 wt% [13]) and the silicate contents of Ni and Co are still about an order of magnitude lower than those observed in the mantle [1,3]. These latter observations effectively exclude single-stage core segregation at low pressure. Recent high pressure data on Ni and Co [1–3,16–20] demonstrate, however, that Ni and Co become less siderophile with increasing pressure and that single-stage core–mantle equilibrium is feasible at pressures above 25 GPa, corresponding to the base of a deep magma ocean [1,2]. According to extrapolations made by Righter and Drake [3], for example, the current concentrations of Fe, Ni, Co, W and P in the silicate Earth can be explained by single-stage equilibration between metal and a hydrous peridotitic melt at 27 GPa and 2250 K and fO_2 conditions slightly below IW. Other authors have suggested higher temperatures and pressures (30–40 GPa) [17–20] and lower oxygen fugacities of about 2 log fO_2 units below IW [19,20]. Despite these differences, all studies based on high pressure data conclude that many of the chemical properties of the mantle are consistent with single-stage core–mantle equilibration at very high pressure. The question to address is therefore whether a single high pressure equilibration event is consistent with Si being the principal light element in the core as proposed by Allègre et al. [10].

Javoy [4], based on geochemical arguments, and Guyot et al. [5], on the basis of EOS measurements on Fe–Si alloys, have predicted that Si solubility in Fe metal increases substantially with increasing pressure. Following preliminary experiments that support this hypothesis [21,22], we have studied the solubility of Si in liquid Fe-rich metal at 2.5–23 GPa and 2023–2673 K over a wide range of oxygen fugacities (Table 1). The results enable us to predict the Si content of liquid metal for different core segregation scenarios and to estimate the conditions under which the core could dissolve significant amounts of Si, e.g. the requisite amount of Si for consistency with the CI chondrite Earth model.

2. Experimental procedure

Liquid Fe metal (containing Si and up to 2.6 wt% S) was equilibrated with silicate melt in the presence of magnesiowüstite and olivine in a piston-cylinder apparatus at 2.5 GPa [13]. The sample powders were contained in MgO capsules, surrounded by crushable alumina and by a cylindrical graphite furnace. Pressed $BaCO_3$ was used as the pressure medium with a thin inner sleeve of silica glass to protect the charge from Ba contamination. All assembly components were fired at 1073 K, with the exception of the capsule, which was dried in a vacuum oven at 473 K overnight, and the graphite furnace, which was not heated. The temperature of the experiments was controlled by a $W_3Re/W_{25}Re$ thermocouple situated directly above the capsule. Pressure was applied gradually over a 10 min period together with a temperature ramp of 170 K/min. The sample was quenched by turning off the power to the graphite furnace.

Experiments at higher pressures were performed in a 1200-tonne multianvil apparatus and involved equilibrating liquid Fe–Ni metal (S-free) with magnesiowüstite in the presence of silicate melt and/or olivine. The sample assembly consisted of an MgO (+5 wt% Cr_2O_3) octahedron (18 and 10 mm edge lengths) containing a $LaCrO_3$ heater. The octahedron was compressed using 32 mm tungsten carbide anvils (Toshiba grade F) with truncation edge lengths of 11 or 5 mm (with 18 and 10 mm octahedra, respectively) and pyrophyllite gaskets. Temperature was monitored with a $W_3Re/W_{25}Re$ thermocouple located axially with respect to the heater and with the junction in direct contact with the MgO capsule. The *P*–*T* uncertainties are estimated to be ±0.5 GPa and ±40 K, respectively. Starting materials were Fe–Ni powders doped with 1–1.5 wt% of Co, V, Cr, Mn, Ti and varying amounts of Si which were added as elements or oxides (see [14,23]). The sample was contained in an MgO capsule, which reacted during the experiment to form magnesiowüstite and, in some cases, the $(Mg,Fe)_2SiO_4$ polymorph olivine (Table 1). In each experiment, the sample was first compressed to the desired pressure; the temperature was then raised at

~100 K/min to the desired run temperature and then held there for 5–20 min. The sample was quenched by switching off the power to the furnace and then slowly decompressed.

After the completion of each experiment, the entire sample assembly was mounted in epoxy, sectioned through the centre of the sample and then polished for electron microprobe analysis. Piston-cylinder samples were analysed using a JEOL 8600 electron microprobe at the University of Bristol and multianvil samples using a CAMECA SX50 electron microprobe at the Bayerisches Geoinstitut.

Experimental and analytical details of the experiments, compositions of starting materials and images of typical run products are given in [13,14,23]. All experimental charges were saturated in (Mg,Fe)O, and contain variable fractions of silicate melt and/or solid silicates (Table 1). Although an $(Mg,Fe)_2SiO_4$ polymorph was not detected in all experimental products (Table 1), we consider that the rapidity with which silica-rich melt and MgO capsule react to form olivine (e.g. < 10 min at 9 and 14 GPa, Table 1) implies that all experiments are very close to saturation, depending on pressure, in olivine, wadsleyite or ringwoodite.

3. Results and discussion

Experimentally determined Si contents of liquid Fe-rich metal are listed, together with experimental conditions, in Table 1. Oxygen fugacities were calculated from the compositions of magnesiowüstite in equilibrium with the quenched liquid metal relative to the iron–wüstite (IW) buffer at the relevant *P*, *T* conditions. Oxygen fugacity is defined, as previously described [13,14,23], by log fO_2 (ΔIW) = 2 log (a_{FeO}/a_{Fe}), where a_{FeO} and a_{Fe} are the activities of FeO in magnesiowüstite and Fe in liquid metal, respectively. Although the oxygen fugacities listed in Table 1 are calculated assuming ideal mixing in both phases, application of low *P*, *T* activity–composition relations in magnesiowüstite and Fe alloy would lead to only small differences in estimated log fO_2.

The solubility of Si is shown as a function of

Table 1
Si contents in quenched liquid metal alloy and conditions of piston-cylinder and multianvil experiments

Run	Pressure (GPa)	SiO_2 in starting mix (wt%)	Si in starting mix (wt%)	Temp. (K)	Oxygen fugacity rel. to IW (log fO_2)	Time (min)	Si in metal (wt%)	Observed run products
MKX2[a]	2.5	22.26	0	2023	−2.75	120	0.01 (0.01)	Met, Mw, Ol, Melt
MKX1[a]	2.5	22.26	1.05[b]	2023	−4.59	120	0.37 (0.01)	Met, Mw, Ol, Melt
MK15[a]	2.5	22.26	1.05[b]	2023	−5.23	120	1.69 (0.01)	Met, Mw, Ol, Melt
MK12a[a]	2.5	22.26	3.78[b]	2023	−6.54	120	7.86 (0.02)	Met–Mw, Ol, Melt
MKX[a]	2.5	22.26	3.78[b]	2023	−6.53	120	8.08 (0.06)	Met, Mw, Ol, Melt
MKX3[a]	2.5	22.26	13.55[b]	2023	−6.67	120	24.39 (0.85)	Met, Mw, Ol, Melt
1558[c]	9	2.17	0	2273	−2.08	16	0.14 (0.01)	Met, Mw, Melt
1358[c]	9	16.99	1.78	2273	−2.7	16	0.44 (0.02)	Met, Mw, Ol, Melt
1483	9	15.29	1.60	2273	−2.92	10	0.39 (0.02)	Met, Mw, Ol, Melt
1500	9	16.65	6.75	2273	−4.16	10	5.79 (0.23)	Met, Mw, Ol, Melt
1194	9	2.24	0	2473	−1.26	16	0.05 (0.01)	Met, Mw
1371	9	2.19	0	2473	−1.39	4	0.07 (0.02)	Met, Mw
1352	9	2.19	0	2473	−1.50	16	0.07 (0.01)	Met, Mw
1210	9	2.19	0	2473	−1.47	16	0.07 (0.02)	Met, Mw, Melt
1383	9	2.19	0	2473	−1.47	8	0.08 (0.01)	Met, Mw
1186[c]	9	2.17	0	2473	−2.06	16	0.13 (0.01)	Met, Mw, Melt
1200[c]	9	16.99	1.78	2473	−2.70	16	0.86 (0.05)	Met, Mw, Melt
1218	9	2.13	3.0	2473	−2.84	16	0.91 (0.15)	Met, Mw, Melt
1203	9	16.34	6.63	2473	−3.58	16	3.95 (0.29)	Met, Mw, Melt
1316	9	16.34	6.63	2473	−3.55	16	4.52 (0.20)	Met, Mw, Melt
1273	18	2.13	3.0	2473	−2.32	7	0.52 (0.02)	Met, Mw, Melt
1334	18	16.99	1.78	2473	−2.87	10	1.21 (0.28)	Met, Mw
1275	18	2.17	0	2473	−2.08	15	0.38 (0.03)	Met, Mw
1285	18	2.24	0	2473	−1.12	16	0.07 (0.01)	Met, Mw
1320	18	16.34	6.63	2473	−3.14	10	3.49 (0.13)	Met, Mw
1520	5	16.65	6.75	2273	−3.92	10	3.34 (0.26)	Met, Mw, Melt
1484	9	15.29	1.6	2073	−2.76	10	0.61 (0.01)	Met, Mw, Ol, Melt
1460	14	16.34	6.63	2473	−3.93	10	4.65 (0.14)	Met, Mw, Ol, Melt
1337	23	16.34	6.63	2473	−2.97	4	3.88 (0.10)	Met, Mw, Melt
1418[c]	9	16.99	1.78	2173	−3.35	16	0.54 (0.04)	Met, Mw, Ol
1457[c]	9	16.99	1.78	2373	−2.71	10	0.69 (0.06)	Met, Mw, Melt
1547[c]	9	16.99	1.78	2573	−2.26	9	0.21 (0.02)	Met, Mw, Melt
1312[c]	9	16.99	1.78	2673	−1.90	12	0.06 (0.02)	Met, Mw, Melt
1554[c]	9	2.17	0	2073	−1.92	20	0.05 (0.01)	Met, Mw
1549[c]	9	2.17	0	2173	−1.83	14	0.07 (0.01)	Met, Mw, Melt

Met = metal liquid, Mw = magnesiowüstite, Ol = Olivine, Melt = silicate liquid.
[a]Results taken from [13] with fO_2 values recalculated assuming ideal mixing properties in metal and magnesiowüstite.
[b]Added as FeSi compounds.
[c]T-dependent experiments from [14].

oxygen fugacity in Fig. 1, where four sets of data, each obtained at constant *P–T* conditions over a range of oxygen fugacities, are plotted. At constant *P* and *T*, Si becomes increasingly soluble in liquid metal with decreasing oxygen fugacity. Si also becomes more soluble in liquid Fe alloy with increasing pressure and temperature at constant fO_2, as shown by the regression lines. The *P–T* range (14.5 GPa, 450 K) of the experiments

shown in Fig. 1 covers a spread of Si solubility of more than two orders of magnitude (e.g. 0.045–5 wt% Si at IW-3.5). The intersections between the horizontal reference line for 7 wt% Si (Fig. 1) and the regression lines yield a range of *P–T–*fO_2 conditions at which metal containing 7 wt% Si would be in equilibrium with mantle phases (e.g. 9 GPa, 2273 K, IW-4.2 and 18 GPa, 2473 K, IW-3.5). For comparison, the shaded area in Fig. 1 shows
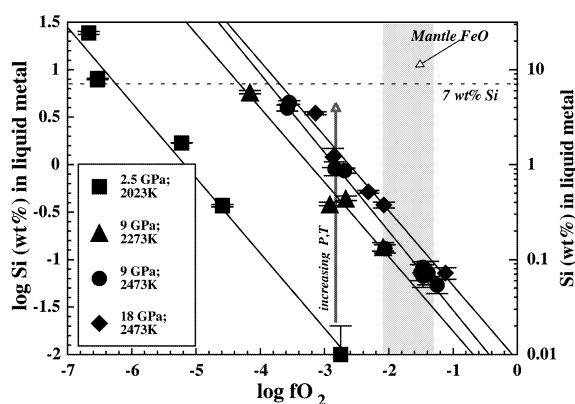
Fig. 1. Experimentally determined Si solubilities in liquid metal as a function of oxygen fugacity at various pressure–temperature conditions. Solid lines are regression lines to data at fixed P and T. The horizontal line indicates the amount of Si (7 wt%) required in the core according to the hypothesis of [10]. At fixed fO_2, the solubility of Si in liquid metal increases with increasing P and T as indicated by the arrow (see text). The grey box indicates redox conditions required for core–mantle equilibrium according to the current FeO content of the mantle (e.g. [15]).

the range of oxygen fugacity values that would generate the current FeO content of the mantle (e.g. [15]). As can be seen, the observed solubility of Si in the metal in the P, T range of the experiments is less than 1 wt% at the oxygen fugacity appropriate for core–mantle equilibrium. However, the trend of increasing solubility of Si with increasing P and T implies that 7 wt% might be approached at pressures and temperatures beyond the range of the experimental data.

In order to facilitate interpretation and extrapolation of the results, a thermodynamic model of Si solubility was fitted to the experimental data. The model is based on the assumption that Fe and Si in the metal mix in the Henry's Law region and that Si activity is thus proportional to mol fraction Si/(Si+Fe). Use of a more complex two-lattice model, which is often employed for S and C in metals, does not, at the concentration range of interest, significantly alter our results and conclusions. Although the presence of other elements in the liquid metal may affect the activity of Si in the metal, the respective composition–activity relations are not known at the high P–T conditions of the present study. Non-ideal mixing effects usu-

ally decrease with increasing temperature, and can therefore be expected to be small at the experimental conditions. Moreover, in the case of S, the metal liquid in experiments performed at 2.5 GPa contains usually less than 0.15 wt% S, except two experiments with 2.41 wt% S (MKX1) and 2.57 wt% S (MKX2 – which was excluded from the fitting described below). Because of the small number of S-bearing experiments used for the thermodynamic model (four 2.5 GPa runs) and the low concentration of S present in them, possible non-ideal mixing effects due to S are expected to be negligible and are omitted in the present study. The effects of small amounts of Si on the melting temperatures of Fe, Co and Ni are all very similar [24] implying that Fe–Si, Co–Si and Ni–Si activity–composition relationships do not differ substantially one from another. This means that the effects of Ni and Co, present at the wt% levels in our experiments, on the activity of Si can be neglected. Results of high pressure experiments of Ito et al. [25] and O'Neill et al. [19] and temperature-dependent results of Gessmann and Rubie [14] were included to extend the database. The latter are also listed in Table 1. The following experiments were omitted when fitting the thermodynamic model: (1) Experiments with Si contents in metal below 0.04 wt%, because of analytical uncertainties (i.e. MKX2). (2) Run MKX3, because of the very high Si content in metal, at which the mixing between Fe and Si may no longer conform to Henry's Law. (3) Run 1245 from [14] because of an anomalously high Si content. In order to be consistent with a silicate mantle containing 8 wt% FeO, results at an oxygen fugacity about 2 log units below IW are required. Therefore, all experimental data were corrected to 2 log fO_2 units below IW by decreasing the Si mol fraction in the metal by 1 log unit for every 1 log unit increase in fO_2 (based on the dependence of Si solubility on fO_2, as determined by [23]) and as required by the equilibrium:

$$\underset{\text{silicate}}{SiO_2} = \underset{\text{metal}}{Si + O_2} \tag{1}$$

The corrected mol fractions of Si were then fitted

as a function of pressure and temperature assuming that they obey the normal thermodynamic relationship for the dissolution reaction 1:

$$RT\ln X_{Si} = -\Delta H° + T\Delta S° - P\Delta V° \qquad (2)$$

where R is the gas constant, T temperature in K, P pressure in GPa, X_{Si} the mol fraction of silicon in liquid metal, $\Delta H°$ the standard enthalpy, $\Delta S°$ the standard entropy and $\Delta V°$ the standard volume change of reaction. The standard enthalpy, entropy and volume change of the dissolution reaction 1 are not absolute values, but are expressed relative to the corresponding values for the IW buffer. They also contain a term, known only at low pressures and temperatures, related to the activity coefficient of Si in the metal. Fitting the data by linear least squares to Eq. 2, the following expression is obtained:

$$RT\ln X_{Si} = -240314 + 37.4 * T + 2305 * P \text{ [in J]}.$$

The observed relative entropy and volume changes are +37.4 J/K and −2.305 cm³/mol (−2305 J/GPa) per mol, respectively. Uncertainties in the regressed values of $\Delta S°$ and $\Delta V°$ are ±23.4 J/K and ±800 J/GPa, respectively, corresponding to ±550 K and ±8.5 GPa uncertainties in temperature and pressure. Although the fitted equation can be safely used to interpolate between the experimental data, confidence in its use to extrapolate the results is strengthened if it can be shown that the derived thermodynamic parameters correspond to independently measured values. We thus need to consider the changes in volume and entropy of appropriate dissolution reactions. The partial molar volume of Si dissolved in Fe was obtained by linear extrapolation from the values for pure Fe and for $Fe_{91}Si_{09}$ given in [26]. This yields a volume of Si in the metal of 5.24 cm³/mol at ambient conditions. All experiments are MgO-saturated and, based on our observations of the speed with which silica-rich melt reacts with the MgO capsule to produce olivine (< 10 min, see above), we consider that all experiments approach saturation in an $(Mg,Fe)_2SiO_4$ polymorph. Thus, the Si content of the metal can, to a good approximation, be treated in terms of the equilibrium:

$$\underset{\alpha/\beta/\gamma}{Mg_2SiO_4} = \quad 2MgO \quad + \quad \underset{metal}{Si} + O_2 \qquad (3)$$
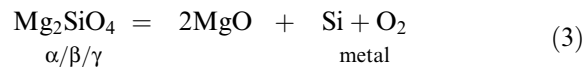
which, for comparison with the experimental results, must be referred to the IW equilibrium:

$$2FeO = 2Fe + O_2 \qquad (4)$$

Using the Si volume discussed above and other volume data for the solids from [27,28] the relative volume change of equilibrium 3 is −5.9 cm³/mol in the field of olivine (α), −2.5 cm³/mol in the field of wadsleyite (β) and −1.6 cm³/mol in the field of ringwoodite (γ). The volume change derived from fitting the experimental solubility data (−2.305 cm³/mol) is in good agreement with these values, reflecting the control exerted on the fit by the highest pressure data lying in the wadsleyite and ringwoodite stability fields.

The entropy change of reaction 3 relative to IW is more difficult to estimate because the entropy of Si dissolved in iron is unknown. If we take the entropies of the pure phases at 1 bar [27,28], the entropy change would be ∼+45 J/K. Bearing in mind the large uncertainty, the entropy change of the reaction fitted to the experimental solubility data (+37.4 J/K) is in good agreement with this value. Despite the uncertainties, therefore, the values of $\Delta S°$ and $\Delta V°$ are in good agreement with tabulated thermodynamic data and enable us to extrapolate the results with some confidence. A test of this supposition is provided by 1 atmosphere thermodynamic data. If we take thermodynamic data for oxides, Mg_2SiO_4 (olivine) and Si at 1800 K from [28] and the activity coefficient of Si in liquid metal from [29] we predict an Si mol fraction in the metal at IW-2 of 1.1×10^{-5}. Our equation, extrapolated to these conditions, gives a mol fraction of 9.5×10^{-6}, well within our quoted uncertainties of the thermochemical value.

Fig. 2 shows the solubility of Si in liquid iron as a function of temperature extrapolated, using our model, to IW-2 and 25 GPa, the approximate pressure at which the current Ni and Co contents of the mantle are postulated to have resulted from metal–silicate equilibrium [1–3]. In order to esti-

mate uncertainties, we considered the quality of fit of Eq. 2 to our data. With the exception of two outliers out of 36 data points, all data (i.e. > 94%) lie within ±27 000 J of the best-fit curve. We therefore used the latter figure to construct maximum and minimum solubilities at 25 GPa, which are shown as dashed lines on Fig. 2. Experimental Si solubility data obtained at P, fO_2 conditions close to IW-2 and 25 GPa [19,25] were recalculated to IW-2 and agree well with the model (Fig. 2).

If we consider that the base of a magma ocean, where core–mantle segregation is postulated to have occurred [1–3], corresponds to a transition from melt to crystal-rich highly viscous mantle, then the temperature must lie between the liquidus and solidus temperatures of the mantle at the appropriate pressure. The phase diagram for KLB-1 peridotite of [30] indicates solidus and liquidus temperatures of about 2600 and 2800 K, respectively, at 25 GPa. Under these conditions, the best fit to our data indicates a solubility of between 0.9 and 1.9 wt% (Fig. 2). Within the uncertainties of the fit, however, solubilities in the range 0.4–6 wt% are possible in this temperature interval. The results demonstrate, therefore, that the single-stage core formation model, at 25 GPa, leads to a significant Si content of the metal (at least 0.4 wt%) and possibly to Si being the major light element in the core (up to 6 wt%).

In order to reach 7 wt% Si in the metal, as required by the CI chondrite hypothesis [10], a temperature of ∼3350 K (±550 K) would be needed at 25 GPa. Assuming that the peridotite phase diagram is correct [30], this temperature lies ∼550 K above the liquidus curve and is therefore unlikely to be reached at the base of a 700 km deep magma ocean. However, 3350 K would be possible at the base of a deeper magma ocean and, indeed, some recent models suggest that metal–silicate segregation occurred at significantly higher temperatures and pressures (e.g. [20]). Our results imply that Si solubility in the metal continues to increase with increasing pressure and temperature until, as shown below, solid perovskite becomes stable. Equilibration near the liquidus of peridotite at higher pressures therefore
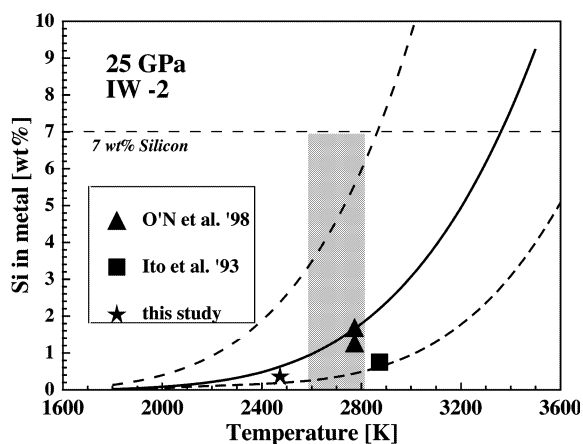

Fig. 2. Calculated Si solubility in liquid metal at 25 GPa and 2 log units below the IW buffer as a function of temperature according to the thermodynamic model (solid line) (see text for details). The two dashed lines indicate the maximum and minimum uncertainties from the regression (94% confidence limit). The horizontal line indicates the amount of Si (7 wt%) required in the core according to [10]. At plausible core formation temperatures (i.e. 2600–2800 K, indicated by the grey box), up to several wt% of Si can be dissolved in liquid metal according to the model. The symbols show experimental solubility results (corrected to IW-2) of O'Neill et al. [19], Ito et al. [25] and this study at pressures close to 25 GPa.

yields a locus of P–T points that would produce 7 wt% Si in the metal as shown in Fig. 3. As can be seen, a temperature of 3150 K at 30 GPa should produce (at IW-2) 7 wt% Si in the metal. Given the range of P–T conditions cited for the deep magma ocean model, these conditions (Fig. 3) appear plausible for production of metal containing 7 wt% Si.

The hypothesis that core formation involved metal segregation at the base of a deep magma ocean is consistent, according to the present results, with several wt% Si dissolving in the liquid metal at an oxygen fugacity of IW-2. It is therefore appropriate to consider the current state of equilibrium between the mantle and a Si-bearing core at the core–mantle boundary (CMB) pressure of 130 GPa. To extrapolate Si solubility to CMB conditions, it is necessary to take account of the transformation of the Mg_2SiO_4 polymorphs of the upper mantle and transition zone to pe-

rovskite and oxide in the lower mantle:

$$Mg_2SiO_4 = MgSiO_3 + MgO \tag{5}$$
$$\alpha/\beta/\gamma \quad \text{perovskite} \quad \text{oxide}$$
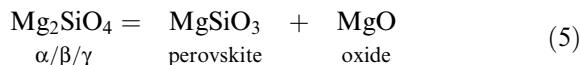
These reactions have negative volume changes [27], irrespective of the Mg_2SiO_4 polymorph, which, when added to the volume change derived from the fit to our experimental results, produce a net volume change for the Si dissolution reaction that must be positive in the lower mantle. Therefore, Si solubility in metal, which increases with pressure in the upper mantle and transition zone, must decrease with increasing pressure in the lower mantle once perovskite is stabilised. Qualitatively the change of sign arises from the change in coordination number of Si in the silicates from 4 (in upper mantle and transition zone phases) to 6 (in perovskite). The magnitude of the effect was calculated by adding the volume change of reaction 5 in the wadsleyite stability field [27] to the volume change of reaction 3 derived from the experimental data. Compressibility, a poorly constrained second order effect, was considered by assuming similar values of K (160 GPa) and K' (4.0) for all solids and by using the third order Birch–Murnaghan equation of state. The calculated solubility of Si in liquid Fe (in equilibrium
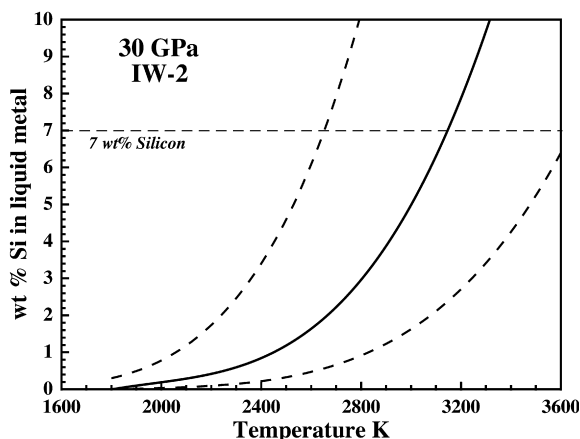

Fig. 3. Calculated Si solubility in liquid metal at 30 GPa and 2 log units below the IW buffer as a function of temperature according to the thermodynamic model (solid line) (see text for details). The two dashed lines indicate the maximum and minimum uncertainties from the regression. The horizontal line indicates 7 wt% Si required in the core according to [10].

with the mantle phases having the appropriate FeO content) at high pressure for the upper and lower uncertainty boundaries of the thermodynamic model (assuming the highest and the lowest $\Delta V°$ of reaction, according to uncertainties) is shown in Fig. 4. These calculations predict a dramatic decrease of Si content in liquid metal with increasing pressure once perovskite is stabilised, i.e. in equilibrium with solid peridotite. At the CMB pressure the model predicts an extremely low Si solubility in metal irrespective of the chosen $\Delta V°$ or the temperature. Note that the results of our thermodynamic model (Figs. 2 and 4) are consistent with the predictions of Javoy [4] and Guyot et al. [5] regarding the effect of pressure on the solubility of Si in liquid metal.

In principle it should be possible to experimentally verify the predictions of Fig. 4 through diamond anvil cell (DAC) experiments. Such results are not yet available due to the difficulty of controlling or constraining the oxygen fugacity in laser-heated DAC experiments. However, the redox conditions of DAC experiments can be estimated qualitatively from the composition of the starting material. An olivine+FeSi starting material, for example, results in much more reducing conditions than an olivine+Fe starting material. Results obtained on the latter starting material by Hillgren and Boehler [31,32] yield up to ~0.2 wt% Si in metal in the pressure range 45–100 GPa, which falls well within the range of Si solubilities predicted by our model (Fig. 4).

As shown in Fig. 4, the solubility of Si in the metal decreases with increasing depth in the lower mantle, due to the increase of the Si coordination number in silicates from 4 to 6 (see also [5]). Therefore, if the core segregated at the base of a magma ocean with a significant Si content, it should now be back-reacting with the mantle, exsolving Si and absorbing Fe from silicates. Progressive reactions of this kind may be responsible, in part, for a chemical boundary layer represented by the D″ layer at the CMB (e.g. [33]). A lower limit on possible chemical boundary layer thickness is obtained by assuming that Si diffusion controls the reaction. Extrapolating Si diffusion data for perovskite at 25 GPa [34] to CMB temperatures (up to 5000 K), diffusion coefficients on
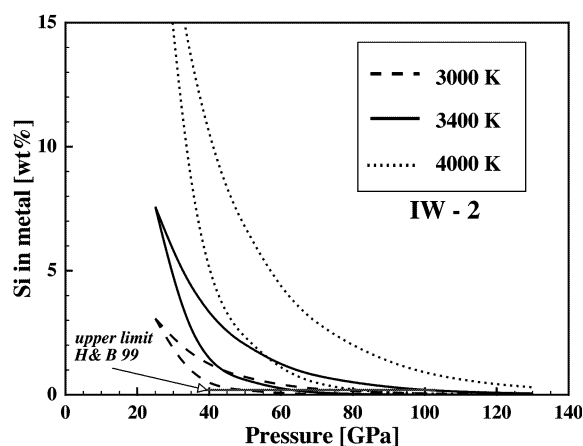
Fig. 4. Calculated Si solubility in liquid metal as a function of pressure according to the upper and lower uncertainty boundaries of the thermodynamic model at 3000, 3400 and 4000 K and $fO_2 = IW-2$. The extrapolation to lower mantle pressures indicates the magnitude of the expected effects: the solubility of Si in liquid metal will dramatically decrease and reach extremely low values at the CMB pressure of 130 GPa. The grey line indicates the upper limit of Si in liquid metal observed by Hillgren and Boehler [32] in DAC experiments with San Carlos olivine+Fe starting material in the pressure range 45–100 GPa, at 10–450 K above the melting temperature of the sample. Oxygen fugacity for these experiments is not known.

the order of 4.9×10^{-16} to 1.1×10^{-13} m²/s are calculated and corresponding diffusion distances of a few tens to one hundred meters in 4 billion years are obtained. At the CMB pressure, Si diffusion is likely to be slower than at 25 GPa, so the estimated values, based on 25 GPa data, are probably upper limits. The formation of such a layer by reaction with (Mg,Fe)O would consume less than 0.001 wt% of Si from the core. A 100 m thick layer is, however, very small compared to the usually reported D″ thickness of 250(±100) km. The latter, if produced by core–mantle reaction, would require infiltration and convective transport. In that case, assuming a peridotitic mantle with 20% magnesiowüstite, the full D″ layer thickness would have extracted about 1 wt% Si from the core by reaction. It seems likely therefore, especially given the unlikely event of convective transport of liquid Fe into the lower mantle on the scale of tens of kilometers [35], that the core has retained most of its Si and that the

latter remains an important component of its inventory of light elements.

Acknowledgements

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